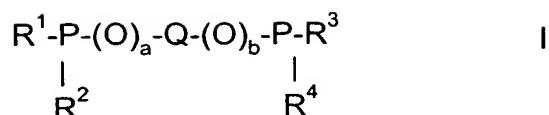


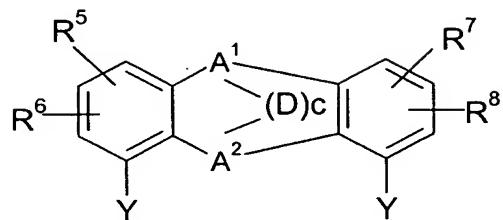
We claim:

1. A process for the continuous preparation of aldehydes having from 5 to 21 carbon atoms by isomerizing hydroformylation in the homogeneous phase of 5 olefin compositions having from 4 to 20 carbon atoms and comprising α -olefins and olefins having internal double bonds by means of synthesis gas in the presence of a homogeneous rhodium catalyst complexed with an oxygen- and/or nitrogen-containing organophosphorus ligand and free ligand at elevated 10 temperature and elevated pressure in a multistage reaction system comprising at least two reaction zones, wherein the olefin composition is firstly reacted with synthesis gas having a CO/H₂ molar ratio of from 4:1 to 1:2 at a total pressure of from 10 to 40 bar in a group of one or more first reaction zones to a conversion of the α -olefins of from 40 to 95% and the hydroformylation mixture from this 15 group of one or more first reaction zones is reacted with synthesis gas having a CO/H₂ molar ratio of from 1:4 to 1:1000 at a total pressure of from 5 to 30 bar in a group of one or more downstream reaction zones, where the total pressure in the one or more downstream reaction zones is in each case from 1 to (T₁-T_f) bar lower than in the preceding reaction zone, where T₁ is the total pressure in the preceding reaction zone and T_f is the total pressure in the reaction zone 20 downstream of the one or more first reaction zones, with the proviso that the difference T₁-T_f is greater than 1 bar, and the CO partial pressure in the one or more downstream reaction zones is in each case lower than in the reaction zone preceding this reaction zone.
- 25 2. A process as claimed in claim 1, wherein a CO/H₂ molar ratio of from 3:2 to 2:3 is set in the one or more first reaction zones and a CO/H₂ molar ratio of from 1:9 to 1:100 is set in the one or more downstream reaction zones.
- 30 3. A process as claimed in claim 1 or 2 which is carried out in two reaction zones.
4. A process as claimed in any of claims 1 to 3, wherein hydrogen-containing offgases from aldehyde and enal hydrogenation processes is used to set the CO/H₂ molar ratio in the one or more reaction zones downstream of the first reaction zones.
- 35 5. A process as claimed in any of claims 1 to 4, wherein the homogeneous hydroformylation catalyst used is a complex of rhodium with a phosphoramidite ligand of the formula I



where

5 Q is a bridging group of the formula



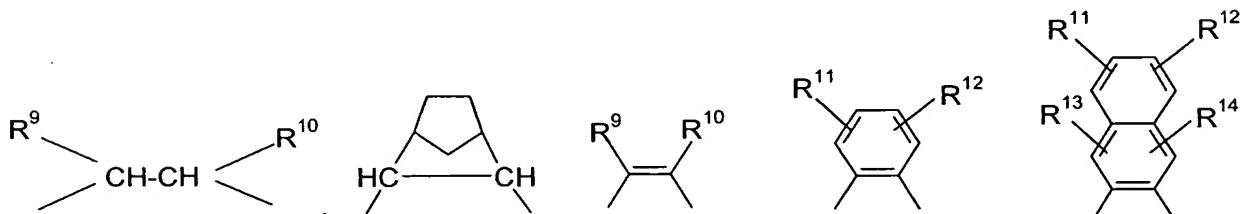
where

10 A¹ and A² are each, independently of one another, O, S, SiR^aR^b, NR^c or CR^dR^e,
where

15 R^a, R^b and R^c are each, independently of one another, hydrogen, alkyl,
cycloalkyl, heterocycloalkyl, aryl or hetaryl,

20 R^d and R^e are each, independently of one another, hydrogen, alkyl, cycloalkyl,
heterocycloalkyl, aryl or hetaryl or together with the carbon atom to which
they are bound form a cycloalkylidene group having from 4 to 12 carbon
atoms or the group R^d together with a further group R^d or the group R^e
together with a further group R^e forms an intramolecular bridging group D,

D is a divalent bridging group selected from among the groups



25

where

R^9 and R^{10} are each, independently of one another, hydrogen, alkyl, cycloalkyl, aryl, halogen, trifluoromethyl, carboxyl, carboxylate or cyano or are joined to one another to form a C_3 - to C_4 -alkylene bridge,

5 R^{11} , R^{12} , R^{13} and R^{14} are each, independently of one another, hydrogen, alkyl, cycloalkyl, aryl, halogen, trifluoromethyl, $COOH$, carboxylate, cyano, alkoxy, SO_3H , sulfonate, NE^1E^2 , alkylene- $NE^1E^2E^{3+}X^-$, acyl or nitro,

10 c is 0 or 1,

10 Y is a chemical bond,

15 R^5 , R^6 , R^7 and R^8 are each, independently of one another, hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl, hetaryl, $COOR^f$, COO^-M^+ , SO_3R^f , $SO_3^-M^+$, NE^1E^2 , $NE^1E^2E^{3+}X^-$, alkylene- $NE^1E^2E^{3+}X^-$, OR^f , SR^f , $(CHR^9CH_2O)_xR^f$, $(CH_2N(E^1))_xR^f$, $(CH_2CH_2N(E^1))_xR^f$, halogen, trifluoromethyl, nitro, acyl or cyano,

20 where

20 R^f , E^1 , E^2 and E^3 are identical or different radicals selected from among hydrogen, alkyl, cycloalkyl and aryl,

25 R^9 is hydrogen, methyl or ethyl,

25 M^+ is a cation,

30 X^- is an anion and

30 x is an integer from 1 to 120,

35 or

35 R^5 and/or R^7 together with two adjacent carbon atoms of the benzene ring to which they are bound form a fused ring system having 1, 2 or 3 further rings,

40 a and b are each, independently of one another, 0 or 1,

40 P is a phosphorus atom,

45 and

45 R^1 , R^2 , R^3 , R^4 are each, independently of one another, hetaryl, hetaryloxy, alkyl, alkoxy, aryl, aryloxy, cycloalkyl, cycloalkoxy, heterocycloalkyl,

5

heterocycloalkoxy or an NE^1E^2 group, with the proviso that R^1 and R^3 are bound via the nitrogen atom of pyrrole groups bound to the phosphorus atom P or R^1 together with R^2 and/or R^3 together with R^4 form a divalent group E which contains at least one pyrrole group bound via the pyrrole nitrogen to the phosphorus atom P and has the formula

10

Py-I-W

where

10

Py is a pyrrole group,

I is a chemical bond or O, S, SiR^aR^b , NR^c or CR^hR^i ,

15

W is cycloalkyl, cycloalkoxy, aryl, aryloxy, hetaryl or hetaryloxy,

and

20

 R^h and R^i are each, independently of one another, hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl or hetaryl,

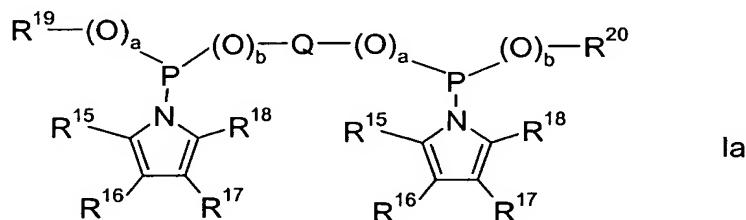
or form a bispyrrole group which is bound via the nitrogen atoms to the phosphorus atom P and has the formula

25

Py-I-Py.

30

6. A process as claimed in any of claims 1 to 5, wherein the homogeneous hydroformylation catalyst used is a complex of rhodium with a phosphoramidite ligand of the formula Ia



where

35

R^{15} , R^{16} , R^{17} and R^{18} are each, independently of one another, hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl, hetaryl, $W'COOR^k$, $W'COO^-M^+$, $W'(SO_3)R^k$, $W'(SO_3)M^+$, $W'PO_3(R^k)(R^l)$, $W'(PO_3)_2(M^+)_2$, $W'NE^4E^5$,

$W'(NE^4E^5E^6)^+X^-$, $W'OR^k$, $W'SR^k$, $(CHR^lCH_2O)_yR^k$, $(CH_2NE^4)_yR^k$, $(CH_2CH_2NE^4)_yR^k$, halogen, trifluoromethyl, nitro, acyl or cyano,

where

5

W' is a single bond, a heteroatom or a divalent bridging group having from 1 to 20 bridge atoms,

10 R^k , E^4 , E^5 , E^6 are identical or different radicals selected from among hydrogen, alkyl, cycloalkyl and aryl,

R^l is hydrogen, methyl or ethyl,

M^+ is a cation equivalent,

15

X^- is an anion equivalent and

y is an integer from 1 to 240,

20 where two adjacent radicals R^{15} , R^{16} , R^{17} and R^{18} together with the carbon atoms of the pyrrole ring to which they are bound may also form a fused ring system having 1, 2 or 3 further rings,

25 with the proviso that at least one of the radicals R^{15} , R^{16} , R^{17} and R^{18} is not hydrogen and R^{19} and R^{20} are not linked to one another,

R^{19} and R^{20} are each, independently of one another, cycloalkyl, heterocycloalkyl, aryl or hetaryl,

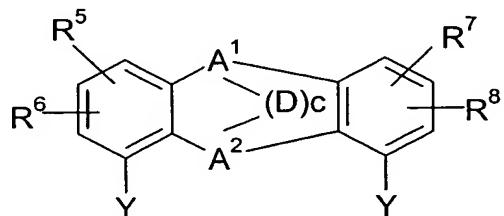
30

a and b are each, independently of one another, 0 or 1,

P is a phosphorus atom,

Q is a bridging group of the formula

35



where

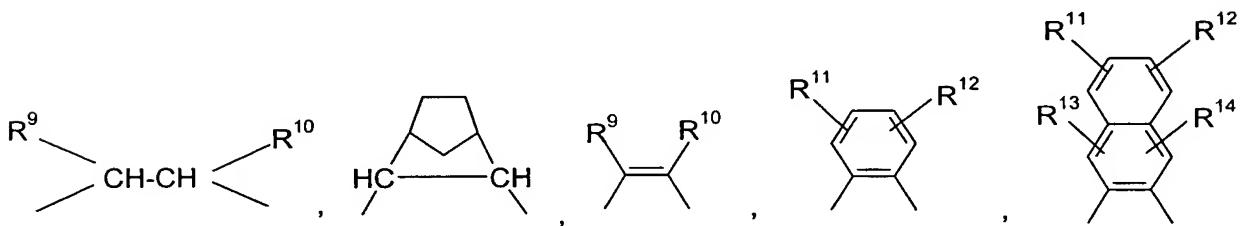
A^1 and A^2 are each, independently of one another, O, S, SiR^aR^b , NR^c or CR^dR^e ,
where

5 R^a , R^b and R^c are each, independently of one another, hydrogen, alkyl,
cycloalkyl, heterocycloalkyl, aryl or hetaryl,

10 R^d and R^e are each, independently of one another, hydrogen, alkyl, cycloalkyl,
heterocycloalkyl, aryl or hetaryl or together with the carbon atom to which
they are bound form a cycloalkylidene group having from 4 to 12 carbon
atoms or the group R^d together with a further group R^d or the group R^e
together with a further group R^e forms an intramolecular bridging group D,

D is a divalent bridging group selected from among the groups

15



where

20 R^9 and R^{10} are each, independently of one another, hydrogen, alkyl, cycloalkyl,
aryl, halogen, trifluoromethyl, carboxyl, carboxylate or cyano or are joined
to one another to form a C_3 - to C_4 -alkylene bridge,

25 R^{11} , R^{12} , R^{13} and R^{14} are each, independently of one another, hydrogen, alkyl,
cycloalkyl, aryl, halogen, trifluoromethyl, COOH , carboxylate, cyano,
alkoxy, SO_3H , sulfonate, NE^1E^2 , alkylene- $\text{NE}^1\text{E}^2\text{E}^{3+}\text{X}^-$, acyl or nitro,

c is 0 or 1,

30 R^5 , R^6 , R^7 and R^8 are each, independently of one another, hydrogen, alkyl,
cycloalkyl, heterocycloalkyl, aryl, hetaryl, COOR^f , COO^-M^+ , SO_3R^f , SO_3^-M^+ ,
 NE^1E^2 , $\text{NE}^1\text{E}^2\text{E}^{3+}\text{X}^-$, alkylene- $\text{NE}^1\text{E}^2\text{E}^{3+}\text{X}^-$, OR^f , SR^f , $(\text{CHR}^9\text{CH}_2\text{O})_x\text{R}^f$,
 $(\text{CH}_2\text{N}(\text{E}^1))_x\text{R}^f$, $(\text{CH}_2\text{CH}_2\text{N}(\text{E}^1))_x\text{R}^f$, halogen, trifluoromethyl, nitro, acyl or
cyano,

35

where

R^f , E^1 , E^2 and E^3 are identical or different radicals selected from among
hydrogen, alkyl, cycloalkyl and aryl,

R^9 is hydrogen, methyl or ethyl,

5 M^+ is a cation,

X^- is an anion and

10 x is an integer from 1 to 120,

or

15 R^5 and/or R^7 together with two adjacent carbon atoms of the benzene ring to which they are bound form a fused ring system having 1, 2 or 3 further rings.

7. A process as claimed in claim 1, wherein the olefin composition used is a raffinate II.

Continuous preparation of aldehydes

Abstract

5

Process for the continuous preparation of aldehydes having from 5 to 21 carbon atoms by isomerizing hydroformylation in the homogeneous phase of olefin compositions having from 4 to 20 carbon atoms and comprising α -olefins and olefins having internal double bonds by means of synthesis gas in the presence of a homogeneous rhodium catalyst complexed with an oxygen- and/or nitrogen-containing organophosphorus ligand and free ligand at elevated temperature and elevated pressure in a multistage reaction system comprising at least two reaction zones, in which the olefin composition is firstly reacted with synthesis gas having a CO/H₂ molar ratio of from 4:1 to 1:2 at a total pressure of from 10 to 40 bar in a group of one or more first reaction zones to a conversion of the α -olefins of from 40 to 95% and the hydroformylation mixture from this group of one or more first reaction zones is reacted with synthesis gas having a CO/H₂ molar ratio of from 1:4 to 1:1000 at a total pressure of from 5 to 30 bar in a group of one or more downstream reaction zones, where the total pressure in the one or more downstream reaction zones is in each case from 1 to (T₁-T_f) bar lower than in the preceding reaction zone, where T₁ is the total pressure in the preceding reaction zone and T_f is the total pressure in the reaction zone downstream of the one or more first reaction zones, with the proviso that the difference T₁-T_f is greater than 1 bar, and the CO partial pressure in the one or more downstream reaction zones is in each case lower than in the reaction zone preceding this reaction zone.